

AN

(12) UK Patent Application (19) GB (11) 2 114 466 A

- (21) Application No **8137579**
(22) Date of filing **12 Dec 1981**
(43) Application published
24 Aug 1983
(51) **INT CL³**
C08J 7/04
(52) Domestic classification
B2E 1747 415T 418T 422T
423T 444T 489S M
C3C 100 101 106 113 136
152 154 184 358 413 414
452 503 550 553 570
U1S 1713 3045 B2E C3C
(56) Documents cited
None
(58) Field of search
B2E
(71) Applicants
Twyford's Limited,
(Great Britain),
Cliffe Vale Potteries,
P.B. Box 23,
Stoke on Trent,
Staffordshire ST4 7AL.
(72) Inventors
Ronald Griffiths
(74) Agent and/or Address for
Service
H. N. and W. S. Skerrett,
Rutland House,
148 Edmund Street,
Birmingham B8 2LQ.

(54) **Manufacture of articles of
reinforced acrylic sheet material**

(57) In a process for manufacturing an article such as a bathtub fabricated from moulded acrylic sheet a shaped shell of the acrylic sheet is reinforced by a layer of glass fibre reinforcement applied using a polyester resin composition incorporating a blowing agent and hollow glass microspheres dispersed therein. The hollow microspheres promote and enhance bonding to the acrylic sheet substrate in the presence of the blowing agent which in turn promotes encapsulation of the reinforcing glass fibres so that no separate "rolling out" operation is needed after application. The hollow microspheres also reduce the density of the reinforced resin material.

GB 2 114 466 A

SPECIFICATION

Manufacture of articles of reinforced acrylic sheet material

5 This invention relates to the manufacture of articles composed of reinforced acrylic sheet material. 5

More specifically, the invention is concerned with articles, for example sanitaryware articles such as bathtubs, which are moulded from acrylic sheet material and reinforced by a layer of glass reinforced resin (GRP) bonded to the acrylic sheet material.

10 The use of acrylic sheet reinforced by a bonded layer of glass fibre reinforced polyester resin is well known in the sanitaryware industry for fabricating hollow sanitaryware articles, such as bathtubs and shower trays for example, and the invention is especially useful in respect of the manufacture of such articles. 10

These sanitaryware articles, such as bathtubs and shower trays, comprise a hollow shell which is commonly fabricated from acrylic sheet using a vacuum forming process to mould the sheet material to the shape required after first heating in an oven to a softening temperature. However, in order to provide 15 sufficient strength and rigidity some additional reinforcement is generally necessary or desirable. This additional reinforcement has been provided in many cases by cladding at least part of the moulded shaped shell of the acrylic sheet material externally with a layer of glass fibre reinforced polyester resin which is 15 applied and bonded to the exterior surface.

Thus, in a conventional manufacturing process, after producing the moulded shaped shell of acrylic sheet material a liquid polyester resin composition mixed, in a mixing head for example, with catalyst and with cut 20 glass fibres or rovings is sprayed over the exterior surface of the shell to build up a covering layer which then has to be rolled out under pressure, in a manual operation using a roller, to spread the reinforcement material evenly, to embed properly all the glass fibres, and to ensure that the material bonds firmly to the acrylic sheet substrate. This operation, however, is not only time-consuming and labour intensive, but the 25 reinforcing layer produced has a relatively high density so that the quantity of material required to provide a layer of adequate thickness with the requisite physical properties is greater than is economically desirable. 25

In order to produce glass fibre reinforced polyester resin material more economically, it has been proposed to incorporate a blowing agent into the resin thereby to foam the material and form a cellular structure of reduced density which has been found to provide an increased stiffness to weight ratio. The 30 foaming effect is also advantageous in glass fibre reinforced polyester material because it further promotes the encapsulation of all the glass fibres without need for the resin to be rolled into the glass in a final rolling out operation. 30

The use of a blowing agent as above mentioned therefore appears to be economically attractive, but if conventional polyester resin compositions used for providing a reinforcing layer on acrylic sheet material 35 are modified merely by incorporating a blowing agent it is found that the foamed material produced does not bond satisfactorily to the acrylic sheet substrate and is liable to become detached therefrom. 35

The present invention, however, enables this problem to be overcome because it has now been found, somewhat surprisingly, that by also incorporating small particles of silicate or glass material into the polyester resin composition a layer of reinforced polyester resin can be produced which will bond 40 satisfactorily to the acrylic sheet substrate. 40

Accordingly, the invention provides a process for the manufacture of articles fabricated from moulded acrylic sheet material comprising the steps of producing a moulded shaped shell of the acrylic sheet material and of then applying to a surface of said shell a liquid polyester resin composition, together with a catalyst or curing agent material and fibre reinforcement material, so as to build up a reinforcing layer, said process 45 being characterised in that the polyester resin composition incorporates a blowing agent which produces a cellular foam structure in the resin during curing and also incorporates a powder of small particles of silicate or glass material dispersed therein in sufficient quantity as to promote and enhance bonding of the reinforced foamed polyester resin layer to the acrylic sheet substrate of said shell. 45

The small particles making up the powder of silicate or glass material are preferably in the form of small 50 microspheres, especially hollow microspheres, having a particle size of less than 500 microns and preferably in the range of 5 to 300 microns. The use of hollow microspheres can also be advantageous from the point of view of providing a filler which further contributes to reduction of the density of the reinforced resin material of the reinforcing layer with an improved stiffness to weight ratio. One such suitable material which is commercially available is that marketed under the trade mark name 'Fillite' by Fillite (Runcorn) Limited of 55 Runcorn, Cheshire, this consisting of a powder of small microspheres within the above-mentioned size range which contain 55-61% by weight of silica (SiO_2) and 26-30% alumina (Al_2O_3) in combination as an aluminosilicate. The amount used will generally be at least one third by weight of the weight of the polyester resin. 55

The polyester resin composition incorporating the blowing agent and silicate or glass particulate filler in accordance with the invention, together with the usual catalyst material and cut glass fibres or rovings, may 60 be applied by spraying in a conventional manner directly on to the surface of the shell of moulded acrylic sheet material, but the foaming effect produced by the blowing agent effectively encapsulates all the glass fibres and an even layer can be obtained which firmly adheres and bonds to the acrylic sheet without pressure such that no subsequent "rolling out" operation is necessary. With an article such as a bathtub 65 which has a turned-over rim or flange, however, the conventional kind of spray gun or spraying head may 65

usefully be modified to permit spraying in different directions within a confined region thereby to enable the whole underside flange area to be covered.

In practice, using a composition in accordance with the invention, it may also be possible advantageously to reduce the length of the reinforcing glass fibres, for example from a length of 12 to 15 mm. as used in a conventional reinforced polyester resin down to 8 to 9 mm., and to use glass roving having fewer strands, that is, having a lower "tex" value. The glass roving is generally drawn continuously into the spraying head where it is cut or chopped into the lengths required by feed rollers and a cutter driven by an air motor, and it may be possible to reduce the normal speed of operation of the air motor so that the glass roving is supplied at a slower rate. All these measures can serve to reduce the amount of glass fibre reinforcement material used, this being possible because of the enhanced strength and physical properties obtained by incorporating the blowing agent and silicate or glass powder in carrying out the invention.

Any suitable blowing agent may be used but a sulphonyl hydrazide blowing agent, such as the material marketed by Uniroyal Inc. under the designation CELOGEN XP-100 (the word "CELOGEN" being a Registered Trade Mark), has been found to be particularly effective.

By way of example, a typical formulation for a reinforcing layer in a process in accordance with the invention for the manufacture of a bathtub fabricated from moulded acrylic sheet material may be as follows:-

| Material | Ingredients | Parts (by Wt.) |
|---|-----------------------------|----------------|
| Liquid polyester resin composition | Unsaturated polyer resin | 100 |
| | 6% cobalt octoate | 1.5 |
| | Copper naphthenate (25 ppm) | 0.0025 |
| Non-ionic surfactant (e.g. Dow Corning 193) | | 2 |
| | Aerosil | 1 |
| | Propylene glycol | 0.5 |
| Stearyl stearate | | 1 |
| | "Celogen" XP-100 | 4 |
| | "Fillite" | 40 |
| Styrene | | 15 |
| Fibrous reinforcement | Glass roving | 50 |
| Catalyst | MEKP Catalyst | 1-2 |

In the above formulation, the cobalt octoate and copper naphthenate are accelerators which respectively control the degree of foaming and length of time for foaming, the surfactant promotes stability of the foam, the "Aerosil" controls the thixotropic characteristics of the resin and is "wetted out" by the propylene glycol, the stearyl stearate assists in preventing residual surface tackiness, and the styrene is a conventional diluent for the resin. The unsaturated polyester resin is an orthophthalic resin, for example the material marketed under the designation STYPOL 40 - 6993 by Freeman Chemicals Limited of Ellesmere Port.

In this example, the formulation is sprayed as previously indicated directly onto the untreated exterior surface of the shell of the bathtub which is produced by a vacuum forming process from acrylic sheet having, for example, a thickness of about 2 mm. The liquid polyester resin composition is supplied to a spraying head wherein it is mixed internally with the MEKP (methyl ethyl ketone peroxide) catalyst close to the discharge point adjacent which it is mixed externally with the glass roving. The glass roving, which is preferably precoated with a size coupling agent such as silane/chrome, is drawn into the spraying head from a continuous source and is cut into lengths (generally 12-15 mm but may be less) by a cutter adjacent the resin discharge nozzle according to a conventional arrangement. As soon as the resin is mixed with the catalyst it starts to foam and the foaming action during discharge from the spraying nozzle encapsulates the glass reinforcing fibres and eliminates any need to roll out the material on the surface of the acrylic sheet shell to which it bonds firmly without the application of external pressure. The thickness of the layer of the foamed reinforced polyester resin built-up on the acrylic sheet substrate will generally be of a similar order to the thickness of the latter but has a relatively low density with a high stiffness to weight ratio.

The reason for the enhanced bonding effect is not fully understood but it is believed that it may possibly involve a keying effect of the hollow microspheres of the "Fillite" powder material with the surface of the acrylic sheet which is likely to soften during the exothermic reaction occurring in the curing stage which proceeds relatively quickly in the presence of the foaming agent.

5 Many modifications may be made within the scope of the invention in the exact make up of the formulation and additional fillers or other materials may be incorporated if desired. Also the invention may be applied to the manufacture of many different kinds of articles fabricated from moulded acrylic sheet material although, as indicated, it is especially suitable for the manufacture of sanitaryware articles such as bathtubs and shower trays.

10 CLAIMS

10

1. A process for the manufacture of an article fabricated from moulded acrylic sheet material comprising the steps of producing a moulded shaped shell of the acrylic sheet material and of then applying to a surface
 15 of said shell a liquid polyester resin composition, together with catalyst or curing agent material and fibre reinforcement material, so as to build up a reinforcing layer, said process being characterised in that the polyester resin composition incorporates a blowing agent which produces a cellular foam structure in the resin during curing and also incorporates particles of silicate or glass powder material dispersed therein effective to promote and enhance bonding of the reinforced foamed polyester resin layer to the acrylic sheet
 20 substrate of said shell.
2. A process as claimed in claim 1 wherein the particles making up the silicate or glass powder material are in the form of small microspheres, preferably hollow microspheres, having a particle size of less than 500 microns.
3. A process as claimed in claim 2 wherein the microspheres have a particle size in the range of 5 to 300
 25 microns.
4. A process as claimed in claim 2 or 3 wherein the microspheres are hollow and contain 55 - 61% by weight of silica (SiO_2) and 26-30% alumina (Al_2O_3) in combination as an aluminosilicate.
5. A process as claimed in any of the preceding claims, in which the quantity of said silicate or glass powder material incorporated in the polyester resin is at least one third by weight of the weight of said resin.
- 30 6. A process as claimed in any of the preceding claims in which the polyester resin composition incorporating the blowing agent and said silicate or glass powder material, together with catalyst material and cut glass fibres or rovings, is applied by spraying directly on to the surface of the shell of moulded acrylic sheet material, said blowing agent acting to produce a foaming effect which effectively encapsulates all the glass fibres and facilitates obtaining an even layer which firmly adheres and bonds to the acrylic sheet
 35 without application of external pressure such that no subsequent "rolling out" operation is necessary.
7. A process as claimed in any of the preceding claims in which the fibre reinforcement material consists of cut glass fibres or rovings having a cut length of less than 12 mm., for example 8 to 9 mm.
8. A process as claimed in any of the preceding claims, in which the blowing agent comprises a sulphonyl hydrazide.
- 40 9. A process as claimed in any of the preceding claims wherein the reinforcement layer is built up by applying to the moulded shaped shell a composition having a formulation substantially in accordance with the example herein described.
10. A process for the manufacture of an article fabricated from moulded acrylic sheet material carried out substantially as herein described in accordance with the example referred to.
- 45 11. An article made of reinforced moulded acrylic sheet material produced by a process as claimed in any of the preceding claims.
12. An article as claimed in claim 11 which is a hollow sanitaryware article, such as a bathtub or shower tray for example.